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14. ABSTRACT This project provides a new materials solution for air-stable moisture-resistant flexible optoelectronics for smart battlewear. Major scientific contributions of this project are: 1) developed new synthetic methods for preparing perfluoroalkylated aromatic compounds that are key to the organic semiconductor industrials; 2) discovered the threshold of aromatic perfluoroalkylation that can make air-stable n-type organic semiconductor materials; 3) revealed a fundamental understanding that leads to controllably formation of solid state materials with desired structure, important for improving charge transport in organic semiconductor devices; 4) elucidate the structure					
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## **Report Title**

### **Fluorinated Materials for Air-stable and Moisture-resistant Flexible Optoelectronics**

#### **ABSTRACT**

This project provides a new materials solution for air-stable moisture-resistant flexible optoelectronics for smart battlewear. Major scientific contributions of this project are: 1) developed new synthetic methods for preparing perfluoroalkylated aromatic compounds that are key to the organic semiconductor industrials; 2) discovered the threshold of aromatic perfluoroalkylation that can make air-stable n-type organic semiconductor materials; 3) revealed a fundamental understanding that leads to controllably formation of solid state materials with desired structure, important for improving charge transport in organic semiconductor devices; 4) elucidate the structure-function relationship of n-type organic semiconductor materials through both experimental and computational approaches; and 5) discovered a new experimental approach to lead to highly photochemically stable organic semiconductor materials which is key to the practical application of flexible organic solar cells. The success of this project brought foremost benefits to national defense applications including: 1) the optoelectronic devices (OSCs and OLEDs) build with these robust materials will be able to operate under extreme environmental condition; 2) providing new materials for power generation (flexible solar cells) and storage in the battle field for individual warrior where other form of power supply and storage is not available.

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
08/28/2012 2.00	Haoran Sun, Anjaneyulu Putta, Michael Billion. Arene Trifluoromethylation: An Effective Strategy to Obtain Air-Stable n-Type Organic Semiconductors with Tunable Optoelectronic and Electron Transfer Properties, The Journal of Physical Chemistry A, (08 2012): 8015. doi: 10.1021/jp301718j
09/14/2013 10.00	Zhihua Wang, Anjaneyulu Putta, Jeffery D. Mottishaw, Qiang Wei, Hua Wang, Haoran Sun. Molecular Origin of Isomerization Effects on Solid State Structures and Optoelectronic Properties: A Comparative Case Study of Isomerically Pure Dicyanomethylene Substituted Fused Dithiophenes, The Journal of Physical Chemistry C, (08 2013): 16759. doi: 10.1021/jp4033029
09/14/2013 14.00	Haoran Sun, Jeffery D. Mottishaw. Effects of Aromatic Trifluoromethylation, Fluorination, and Methylation on Intermolecular $\pi$ - $\pi$ Interactions, The Journal of Physical Chemistry A, (08 2013): 0. doi: 10.1021/jp403679x
09/14/2013 13.00	H. Sun, Q. Wei. Polyfluorinated Electrolyte Solutions and Additives for High Voltage Non-Flammable Lithium Batteries, ECS Transactions, (07 2013): 349. doi: 10.1149/05026.0349ecst
09/14/2013 12.00	Jeffery D. Mottishaw, Dmitri Kilin, Hai-Ping Cheng, Valentin Karasev, Qi Hua Fan, Haoran Sun. Elucidating the role of non-radiative processes in charge transfer of core-shell Si:SiO <sub>2</sub> , Molecular Physics, (09 2013): 0. doi: 10.1080/00268976.2013.836606
11/21/2012 6.00	Haoran Sun, Usha K. Tottempudi, Jeffery D. Mottishaw, Prem N. Basa, Anjaneyulu Putta, Andrew G. Sykes. Strengthening $\pi$ - $\pi$ Interactions While Suppressing Csp <sup>2</sup> H $\cdots$ $\pi$ (TShaped) Interactions via Perfluoroalkylation: A Crystallographic and Computational Study That Supports the Beneficial Formation of 1D $\pi$ - $\pi$ Stacked Aromatic Materials, Crystal Growth & Design, (11 2012): 5655. doi: 10.1021/cg301151u
11/21/2012 7.00	Haoran Sun, Anjaneyulu Putta, Justin P. Kloster, Usha K. Tottempudi. Unexpected photostability improvement of aromatics in polyfluorinated solvents, Chemical Communications, (11 2012): 12085. doi: 10.1039/c2cc35591d
12/30/2013 19.00	Anjaneyulu Putta, Jeffery D. Mottishaw, Zhihua Wang, Haoran Sun. Rational Design of Lamellar $\pi$ - $\pi$ Stacked Organic Crystalline Materials with Short Interplanar Distance, Crystal Growth & Design, (11 2013): 0. doi: 10.1021/cg401637a
<b>TOTAL:</b>	<b>8</b>

Number of Papers published in peer-reviewed journals:

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(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

### (c) Presentations

- [1] Miles D. Koppang, Jordan H. Kramer, Adam R. Erck, Haoran Sun, Anjaneyulu Putta, Jeffery D. Mottishaw, Ferrocene tagging of amines: an alternative approach using haloferrocenes. Abstracts, 48th Midwest Regional Meeting of the American Chemical Society, Springfield, MO, United States, October 16-19, MWRM-18 (2013).
- [2] Haoran Sun, Mohammad O. BaniKhaled, Usha K. Tottempudi, Jeffery D. Mottishaw, Perfluoroalkylated heteroaromatic ligands and their metal complexes with square planar structures for n-type organic semiconductor materials. Abstracts, 48th Midwest Regional Meeting of the American Chemical Society, Springfield, MO, United States, October 16-19, MWRM-300 (2013).
- [3] Haoran Sun, Anjaneyulu Putta, Jeffery D. Mottishaw, Perfluoroalkylated supramolecular synthons. Abstracts, 48th Midwest Regional Meeting of the American Chemical Society, Springfield, MO, United States, October 16-19, MWRM-144 (2013).
- [4] Haoran Sun and Michael Billion, Tuning optical and electronic properties of arene-based organic semiconductors via perfluoroalkylation, ORGN 919, 240th ACS National Meeting & Exposition, August 22-26, 2010, Boston, MA.
- [5] Haoran Sun, Anjaneyulu Putta, and Justin Kloster, Synthesis of air-stable, moisture-resistant, and tunable perfluoroalkylated arenes for optoelectronics, ORGN 731, 240th ACS National Meeting & Exposition, August 22-26, 2010, Boston, MA.
- [6] Anjaneyulu Putta and Haoran Sun, Arene perfluoroalkylation: a molecular design strategy for searching air-stable and photostable n-type organic semiconductors, South Dakota EPSCoR meeting, June 2012.
- [7] Usha K. Tottempudi and Haoran Sun, Toward high performance organic semiconductor materials: insights from crystal structure analysis and NMR spectral study on intermolecular pi-pi interaction, South Dakota EPSCoR meeting, June 2012.
- [8] Jeffery D. Mottishaw and Haoran Sun, Origin of enhanced intermolecular pi-pi interaction in trifluoromethylated aromatics: computational study with the Moller-Plessett (MP2) method, South Dakota EPSCoR meeting, June 2012.
- [9] Sun, Haoran, Effects of direct ring fluorination and perfluoroalkylation on optical and electronic properties of aromatics From Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011 (2011), FLUO-22. Language: English, Database: CAPLUS
- [10] Sun, Haoran; Tottempudi, Usha K.; Yang, Changying, Synthesis, characterization, and proton affinity of electron deficient phenanthrolines. From Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011 (2011), FLUO-20. Language: English, Database: CAPLUS
- [11] Sun, Haoran; Putta, Anjaneyulu; Kloster, Justin; Billion, Michael; Mottishaw, Jeffery, Improve photostability of organic semiconductor materials via perfluoroalkylation. From 20th Winter Fluorine Conference, American Chemical Society, Division of Fluorine Chemistry, St. Pete Beach, FL, United States, January 9-14 (2011), FLUO-78. Language: English, Database: CAPLUS
- [12] Sun, H.; Mottishaw, J. D.; Putta, A. Effects of aromatic perfluoroalkylation on weak non-covalent intermolecular interactions: Insight for rational design of high performance n-type organic semiconductor materials. Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, September 8-12, 2013 2013, COMP-302.
- [13] Sun, H. Perfluoroalkylation strengthening lamellar  $\pi$ - $\pi$  stacked structure in n-type organic semiconductor materials: Coherent enhancement of  $\pi$ - $\pi$  and Csp<sup>3</sup>-F $\cdots$ F-Csp<sup>3</sup> interactions. 21st Winter Fluorine Conference, American Chemical Society, Division of Fluorine Chemistry, St. Pete Beach, FL, 2013, FLUO-86.
- [14] Putta, A.; Sun, H. Synthesis and characterization of perfluoroalkylated N-heteroacene-based n-type organic semiconductor materials. Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April 7-11, 2013 2013, ORGN-685.
- [15] Mottishaw, J. D.; Sun, H. Effect of perfluoroalkylation on weak non-covalent intermolecular interactions between arenes: A computational study on selected aromatic systems. Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April 7-11, 2013 2013, PHYS-403.
- [16] Anjaneyulu Putta, Usha K. Tottempudi, Justin P. Kloster, Jeffery D. Mottishaw, Zhihua Wang, Andrew G. Sykes and Haoran Sun, Crystal engineering of n-type organic semiconductor materials through perfluoroalkyl tails, South Dakota EPSCoR meeting, June 2013.
- [17] Haoran Sun, Weak non-covalent interactions bridge molecular design and functional materials, South Dakota EPSCoR meeting, June 2013.
- [18] Qiang Wei and Haoran Sun, Polyfluorinated Electrolyte Solutions and Additives for High Voltage Non-Flammable Lithium Batteries, South Dakota EPSCoR meeting, June 2013.
- [19] Jeffery D. Mottishaw, Mukul Dubey, Dmitri Kilin, Qi Hua Fan, and Haoran Sun, Calculating Electronic Properties of the Si:SiO<sub>2</sub> Interface Using Density Functional Theory with Periodical Boundary Conditions, IEEE meeting presentation, Rapid City, SD, May 7, 2013
- [20] Zhihua Wang, Anjaneyulu Putta, Jeffery D. Mottishaw, Qiang Wei, and Haoran Sun, The molecular origin of isomerization effects on solid state structures and optoelectronic properties: a comparative case study of isomeric pure dicyanomethylene substituted fused dithiophenes, South Dakota EPSCoR meeting, June 2013.
- [21] Jeffery D. Mottishaw and Haoran Sun, Effects of aromatic trifluoromethylation, fluorination, and methylation on pi-pi stacked and T-shaped interactions, South Dakota EPSCoR meeting, June 2013.
- [22] Jenny Sun and Miles Koppang, Electrochemical Characterization of Air Stable Donor Acceptor Monomers, USD Undergraduate Research Summer Symposium, Ponca, NE, July 30, 2013.
- [23] Matthew Kibler, Anjaneyulu Putta, and Haoran Sun, Synthesis of Asymmetric n-type Semiconductors through Perfluoroalkylation of Pyrene Derivatives, USD Undergraduate Research Summer Symposium, Ponca, NE, July 30, 2013.
- [24] Jeffery Mottishaw, Dmitri Kilin, Hai-Ping Cheng, Valentin Karasev, Haoran Sun and Qi Hua Fan, Elucidating the role of non-radiative processes in charge transfer of model core-shell Si:SiO<sub>2</sub> nanoparticles, the 53th Sanibel Symposium, Feb. 2013.

Number of Presentations: 24.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

08/28/2012    3.00    Haoran Sun, Qiang Wei. Polyfluorinated electrolyte solutions and additives for high voltage non-flammable lithium batteries, Meet. Abstr. 2012, Volume MA2012-02, Issue 12, Pages 1230.. 07-OCT-12, . : ,

**TOTAL:      1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

08/28/2012    4.00    Haoran Sun, Anjaneyulu Putta, Justin P. Kloster, Usha K. Tottempudi. Unexpected Photostability Improvement of Aromatics in Polyfluorinated Solvents, Chem. Commun. (08 2012)

08/28/2012    5.00    Usha K. Tottempudi, Jeffery D. Mottishaw, Prem N. Basa, Haoran Sun, Anjaneyulu Putta, Andrew G. Sykes. Strengthening ??? Interactions while Suppressing CHsp<sup>2</sup>•••pi(T-Shaped) Interactions via Perfluoroalkylation: A Crystallographic and Computational Study that Supports the Beneficial Formation of 1-D pi-pi Stacked Aromatic Materials, Crystal Growth & Design (08 2012)

11/21/2012    8.00    Haoran Sun, Qiang Wei. Polyfluorinated Electrolyte Solutions and Additives for High Voltage Non-Flammable Lithium Batteries, ECS Transactions (11 2012)

**TOTAL:      3**

**Number of Manuscripts:**

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**Books**ReceivedPaper**TOTAL:****Patents Submitted**

1. ELECTRON-DEFICIENT FLUOROUS PORPHYRINS AND METHODS OF MAKING AND THEIR USE IN ORGANIC SOLAR CELLS, US20130206231A1
2. FLUORINATED AROMATIC MATERIALS AND THEIR USE IN OPTOELECTRONICS, US20120208989A1

**Patents Awarded**

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**Awards**

- 1) Justin Kloster, Distinguished Undergraduate Senior Award in Chemistry, Awarded by The American Chemical Society (ACS) Sioux Valley Local Section, May, 2011.
- 2) Graduate student Usha K. Tottempudi, the University of South Dakota graduate school research grant award, December 2011.
- 3) Graduate student Anjaneyulu Putta, the University of South Dakota graduate school research grant award, December 2011.

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Anjaneyulu Putta	0.20	
Justin Kloster	0.10	
<b>FTE Equivalent:</b>	<b>0.30</b>	
<b>Total Number:</b>	<b>2</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Zhihua Wang	0.20
Gang Yang	0.20
Fengrong Dai	0.20
Jayesh Govani	0.10
Guojian Wang	0.10
<b>FTE Equivalent:</b>	<b>0.80</b>
<b>Total Number:</b>	<b>5</b>

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### **Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

**FTE Equivalent:**

**Total Number:**

---

### **Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

**FTE Equivalent:**

**Total Number:**

### **Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 3.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

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### **Names of Personnel receiving masters degrees**

<u>NAME</u>
-------------

Justin Kloster

**Total Number:** 1

---

### **Names of personnel receiving PHDs**

<u>NAME</u>
-------------

Anjaneyulu Putta

**Total Number:** 1

---

### **Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

**FTE Equivalent:**

**Total Number:**

---

**Sub Contractors (DD882)**



## **Inventions (DD882)**

### **5 Synthesis of electron-deficient fluorinated porphyrins for use in organic solar cells**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Haoran Sun

5f-1a: University of South Dakota

5f-c: 414 E. Clark St.

Vermillion

SD 57069

### **5 FLUORINATED AROMATIC MATERIALS AND THEIR USE IN OPTOELECTRONICS**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Haoran Sun

5f-1a: University of South Dakota

5f-c: 414 E. Clark St.

Vermillion

SD 57069

## **Scientific Progress**

See attachment for detailed Scientific Progress and Accomplishments.

## **Technology Transfer**

## Scientific Progress and Accomplishments

### Fluorinated Materials for Air-stable and Moisture-resistant Flexible Optoelectronics

*Haoran Sun,*

*Department of Chemistry, University of South Dakota, Vermillion, SD, 57069*

#### Abstract

This project provides a new solution for producing air-stable moisture-resistant flexible optoelectronics for smart battlewear. **The major scientific contributions of this project** are: 1) developed new synthetic methods for preparing perfluoroalkylated aromatic materials that are key to the organic semiconductor industrials; 2) discovered the critical threshold of the degree of aromatic perfluoroalkylation that can make air-stable n-type organic semiconductor materials; 3) revealed a fundamental understanding that leads to controllably formation of solid state materials with desired structure, important for improving charge transport in organic semiconductor devices; 4) elucidate the structure-function relationship of n-type organic semiconductor materials through both experimental and computational approaches; and 5) discovered a new experimental approach to lead to highly photochemically stable organic semiconductor materials which is key to the practical application of flexible organic solar cells. The success of this project brought foremost **benefits to national defense applications** including: 1) the optoelectronic devices (OSCs and OLEDs) build with these robust fluorinated materials will be able to operate under extreme environmental condition; 2) providing new materials for power generation (i.e. flexible solar cells) and storage in the battle field for individual warrior where other form of power supply and storage is not available. **The long term impact** of this project to the scientific community and national defense applications includes 1) the development of new type of organic semiconductor materials; 2) the creation of research infrastructure for flexible optoelectronics for defense applications; and 3) work force development for national defense R&D.

## Table of Contents

Abstract	1
Table of Contents	2
List of Appendixes, Illustrations and Tables	3
Statement of the problem studied	4
Summary of the most important results	5
Bibliography	8

## **List of Appendixes, Illustrations and Tables**

Figure 1. Estimated reduction potentials of various CF<sub>3</sub> substituted anthracenes.

Figure 2. Discovery of solution process-able and photochemical stable organic semiconductor materials.

Figure 3. Crystal engineering through aromatic perfluoroalkylation (left). Picture on the right: computational results show preferential  $\pi$ - $\pi$  stacked interaction over T-shaped interaction.

Figure 4. Comparison of electron affinities (EAs) and ESP maps of various N- and S-containing heterocycles with similar frames but different heteroatoms and substitutions on the rings.

Figure 5. Molecular packing of non-substituted (left), mono-perfluorobutyl substituted (middle), and bis-perfluorobutyl substituted benzophenazines. Dotted blue lines indicate short contact between adjacent molecules.

Figure 6. Molecular orbital overlapping in dimer molecules of bis-perfluorobutylated dithiophenazine.

## Statement of the problem studied

This project addresses the national defense's critical needs in developing flexible optoelectronics for next generation battlewear for warfighters. Our research results proofed that the unique properties of fluorinated materials including high thermal and photochemical stability, resistance to oxidation and moisture permeation, in fact, benefit the development of a new generation of flexible optoelectronics through the discovery of new n-type organic semiconductor materials. Furthermore, the electronic and optical properties of these new optoelectronic materials are found to be tunable over large range by aromatic perfluoroalkylation. Aromatic perfluoroalkylation further provides excellent opportunity to discover novel functional materials for military applications. The success of this research project also provided necessary workforce development for research and development needs in national defense through significant training for students at all levels in organic semiconductor and optoelectronic fields.

**Background on scientific problems and strategies:** The discovery of high performance air-stable n-type organic semiconductor materials is critical for many electronic and optoelectronic device applications.<sup>1</sup> Air-stability (including moisture-resistance) and electron mobility are two key factors that currently limit the wide deployment of n-type organic semiconductor devices including organic field effect transistors (OFETs)<sup>2</sup>, organic solar cells (OSCs)<sup>3</sup>, and organic light emitting diodes (OLEDs)<sup>4</sup>. Despite great progress in p-type organic semiconductor research<sup>3a,5</sup>, developing high performance air-stable n-type organic semiconductor materials remains a significant obstacle.<sup>6</sup> Air-stability of n-type organic semiconductor devices is thermodynamically determined by the difference in oxygen reduction potentials and the first reduction potential of the corresponding semiconductor materials (in many cases, researchers also use electron affinities (EAs) or LUMO energies to estimate the air-stability of these materials).<sup>1e,7</sup> The fundamental physicochemical reason behind the air (oxygen, moisture) instability of those n-type organic semiconductor devices is that oxygen, together with water (as a proton source), oxidizes the n-channel semiconductor transporter—an electron in semiconductor terms or a radical anion in chemistry terms—while the device is in operation.<sup>8</sup> In principle, if an n-type organic semiconductor material's first reduction potential is higher than the oxygen reduction potentials, the device constructed with this material will be thermodynamically air-stable.<sup>9</sup>

One strategy to making air-stable n-type semiconductors is addition of electron-withdrawing substituents onto aromatic rings to shift the first reduction potential to a more positive value than the oxygen reduction potentials.<sup>10</sup> The other strategy is to avoid water (a proton source) involvement, forcing oxygen to only go through a one-electron reduction which has a much lower reduction potential. Thus, fewer electron-withdrawing substituents are needed to shift the first reduction potential more positive than the oxygen reduction potential. In principle, both strategies should be able to generate air-stable n-type organic semiconductors; however the former strategy possesses significant synthetic burdens in practice and may be impossible to overcome because of the challenges of adding multiple electron withdrawing groups. F, CN, NO<sub>2</sub>, COOR, CONR<sub>2</sub>, CF<sub>3</sub>, C<sub>n</sub>F<sub>2n+1</sub> are commonly used in making n-type semiconductors, with some of them being air-stable.<sup>1h,5a,11</sup> While direct fluorination on the aromatic ring (sp<sup>2</sup>-carbon) only introduces a moderate electron-withdrawing effect ( $\sigma_p$  value for fluorine is 0.06)<sup>12</sup>, in contrast, perfluoroalkyl substitution introduces much greater electron-withdrawing ability ( $\sigma_p$  value for CF<sub>2</sub>CF<sub>3</sub> is 0.52)<sup>12</sup>. Furthermore, the perfluoroalkyl substitutes possess superhydrophobicity<sup>13</sup>, oleophobicity<sup>13</sup>, and fluorophilicity<sup>14</sup> which could potentially increase the barrier of electron transfer (ET) between oxygen and semiconductor materials to provide kinetic stability of the semiconductor devices.<sup>15</sup>

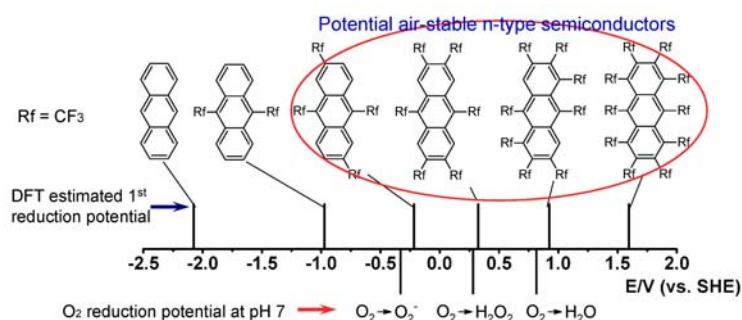
In this project, through both computational and experimental approaches, we successfully discovered and developed a series of perfluoroalkylated aromatics that chemically and photochemically stable and with controllable solid state structure. The very short  $\pi$ - $\pi$  distances we discovered in N- and S-containing

perfluoroalkylated aromatics lead to excellent molecular orbital overlapping between adjacent molecules in the solid state. This built a sound materials foundation for high efficient organic semiconductor devices.

## Summary of the most important results

### 1). Discovered the threshold of aromatic perfluoroalkylation that can make air-stable n-type organic semiconductor materials (H. Sun et al J. Phys. Chem. A 2012).<sup>7c</sup>

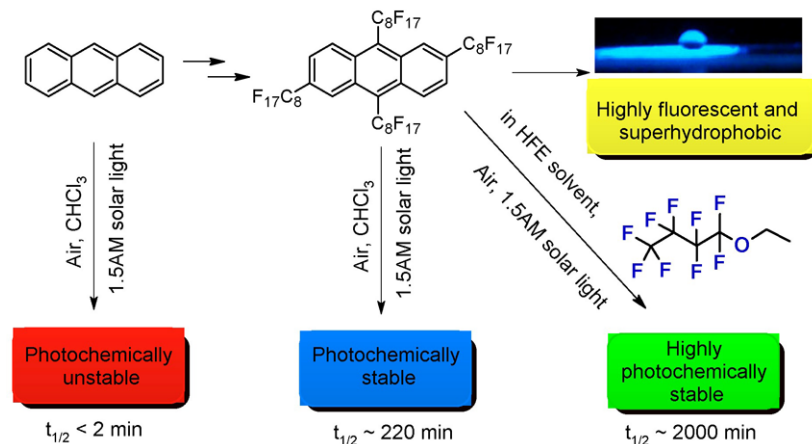
A systematic computational study from our group has demonstrated that trifluoromethylation can modulate the first reduction potential over a very large range, leading to thermodynamically air-stable organic semiconductors. Further, perfluoroalkyl groups, with similar electron-withdrawing ability but better superhydrophobicity and oleophobicity compared to trifluoromethyl, can lead to a synthetically practical route to air-stable organic semiconductors as shown in Figure 1. Because the perfluoroalkyl chains could form a barrier to stop water (a proton source) from attacking the aromatic core, the radical anion of anthracene with four perfluoroalkyl groups could become thermodynamically air-stable since its first reduction potential is more positive than the one-electron reduction potential of oxygen.



**Figure 1.** Estimated reduction potentials of various  $CF_3$  substituted anthracenes.<sup>7c</sup>

### 2). Discovered solution process-able and highly photochemical stable organic semiconductor materials (H. Sun et. al. Chem. Comm. 2012).<sup>16</sup>

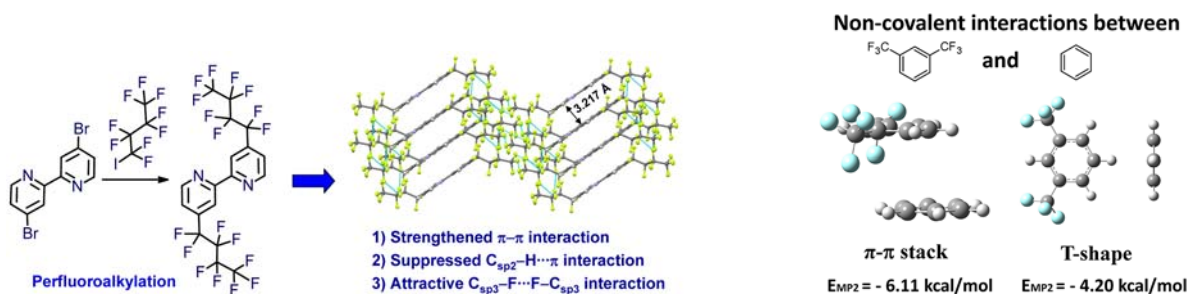
The excellent fluorophilicity and oleophobicity of perfluoroalkyl groups provides a route for orthogonal solution-processing of perfluoroalkyl functionalized organic semiconductor materials.<sup>17</sup> Perfluoroalkylated organic materials have poor solubility in hydrocarbon-based organic solvents (both polar and non-polar solvents). However, they are soluble in heavily fluorinated solvents such as 3M Novec engineering fluids HFE-7100®, HFE-7200®, and HFE-7500®.<sup>5s,17c</sup> For example, tetra-perfluorooctyl anthracene is almost insoluble in chloroform and insoluble in DMSO and DMF, but it is very soluble in HFE-7200 up to 10 mg/ml at room temperature.<sup>16</sup> This significant solubility change from hydrocarbon-based solvents to heavily fluorinated solvents provides us with an excellent opportunity for orthogonal solution processing of perfluoroalkylated organic semiconducting materials.<sup>17b</sup> The materials are also highly photochemical stable (Figure 2). After perfluoroalkylation and use of fluorinated solvents, the photostability of aromatics tested in our lab increases over thousand times.



**Figure 2.** Discovery of solution process-able and photochemical stable organic semiconductor materials.

### 3). Control material solid state structure through modulating molecular structure and perfluoroalkylation (J. Mottishaw et.al. J. Phys. Chem. C. 2013; H. Sun et.al. Cryst. Growth & Design, 2012)<sup>18</sup>

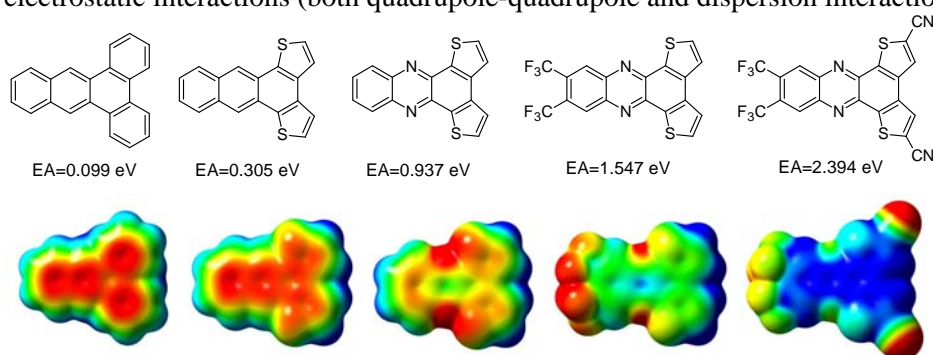
In addition to modulating HOMO, LUMO, band-gap, IPs, EAs, and inner sphere reorganization energy parameters of aromatic compounds at the molecular level, we found that perfluoroalkylation further affects molecular packing in solid state. Our recent results show that perfluoroalkylation of aromatics is a promising strategy to form  $\pi$ - $\pi$  stacked lamellar structure in the solid-state.<sup>18a</sup> As shown in Figure 3, we observed that the formation of lamellar  $\pi$ - $\pi$  stacked structure occurred after perfluoroalkylation of bipyridine molecule. In solid state structures, perfluoroalkyl groups stick together, similar to what has been observed in perfluoroalkyl phosphate compounds reported by Baker's group recently.<sup>19</sup> This, perhaps, is not a surprise when we compare this fluoroalkyl chain aggregation behavior to the phase separation between fluorocarbon and hydrocarbon.<sup>20</sup> Indeed, we could call this fluorocarbon chains separation from hydrocarbon aromatics as **"Phase separation at a molecular level"**. This observation is consistent with available crystal structural data and can be understood from *ab initio* quantum mechanical calculations of non-covalent intermolecular interactions between fluorocarbons and hydrocarbons.<sup>21</sup> The observed short  $\pi$ - $\pi$  distance is also in line with our recent computational results, that interaction energy between adjacent aromatic rings increases with trifluoromethylation, which causes increased quadrupole moment of the molecule.<sup>18b</sup> Thus, preferential formation of  $\pi$ - $\pi$  stacked structure over T-shaped molecular packing can be realized (Figure 3).



**Figure 3.** Crystal engineering through aromatic perfluoroalkylation (left).<sup>18a</sup> Picture on the right: computational results show preferential  $\pi$ - $\pi$  stacked interaction over T-shaped interaction.<sup>18b</sup>

**4). Discover new organic semiconductor materials with very short  $\pi$ - $\pi$  distance in the solid state (A. Putta, et. al. Cryst. Growth & Design, 2013)<sup>22</sup>**

N- and S-containing aromatics are widely studied in literature ranging from ligands for catalytic reactions to pharmaceutically active compounds.<sup>23</sup> Many N-containing aromatics are used as air-stable n-type semiconductors.<sup>24</sup> Heterocycles containing sulfur atoms have often been used as p-type semiconductor materials because of the electron-rich nature of the sulfur stabilizing the radical cation.<sup>25</sup> Heterocycles containing both S and N, such as benzothiazole, become the basic chromophore core for polymer-based semiconductor materials.<sup>26</sup> Introduction of N- and S-containing rings into aromatic compounds leads to significant changes in HOMO and LUMO energies, IPs, EAs, and charge distribution as reflected on the electrostatic surface potential maps (Figure 4). The introduction of N and S brings up two benefits: one is to increase the EAs leading to air-stable organic semiconductor materials; the other is to change the charge distribution pattern along the aromatic  $\pi$  surface, which leads to potentially stronger electrostatic interactions (both quadrupole-quadrupole and dispersion interactions).

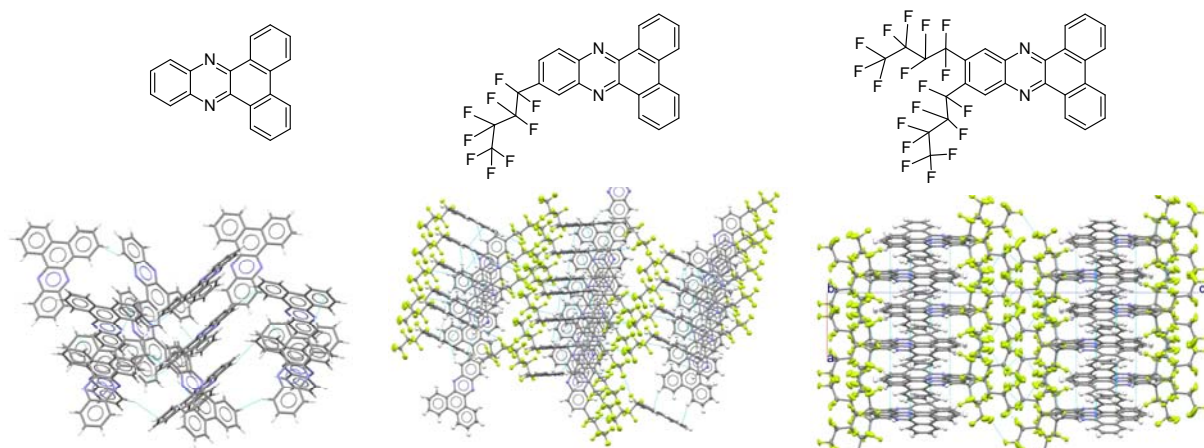


**Figure 4.** Comparison of electron affinities (EAs) and ESP maps of various N- and S-containing heterocycles with similar frames but different heteroatoms and substitutions on the rings.

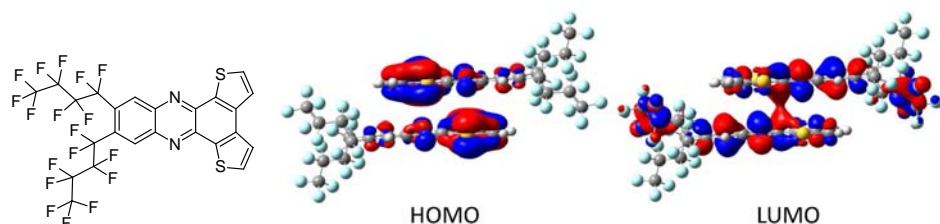
We further found that the degree of perfluoroalkylation is critical to the formation of  $\pi$ - $\pi$  stacked lamellar structure when comparing the structures of mono-perfluorobutyl and bis-perfluorobutyl benzophenazines. Though mono-perfluoroalkylation provides  $\pi$ - $\pi$  stacked structure in the solid state, it forms T-shaped packing as well because of lack of sufficient  $C_{sp^3}-F \cdots F-C_{sp^3}$  interactions, which could steer the molecule packing orientation (see Figure 5). Bis-perfluorobutyl substitution leads to anti-parallel  $\pi$ - $\pi$  stacking with no T-shaped interaction in the crystal structure, though it is not a perfect flat lamellar structure. This structure changing trend suggests that both an electron-steric effect and  $C_{sp^3}-F \cdots F-C_{sp^3}$  attractive interactions play a role in designing materials with  $\pi$ - $\pi$  stacked lamellar structure. Furthermore, by changing the length of the perfluoroalkyl chain, we observed a fine tuning effect on  $\pi$ - $\pi$  stacking distance.

When sulfur atoms are introduced into the aromatic ring with similar shape to benzophenazine, perfect  $\pi$ - $\pi$  stacked lamellar structures are formed with a  $\pi$ - $\pi$  distance of 3.247 Å. Here, though the radius of the sulfur atom is larger than that of the carbon and nitrogen atoms, the softness of sulfur atom provides better polarizability. When the S atom is close to the electronegative nitrogen, induced-polarization interaction (dispersion force) between the two adjacent molecules further strengthens  $\pi$ - $\pi$  stacking. Our DFT-D calculation (B97D/TVZ level of theory) shows that this sulfur containing compound has over 2 kcal/mol more stabilization energy than that of non-sulfur containing analog compound. This clearly demonstrates the benefit of introducing sulfur into the aromatic ring to modulating crystal packing. Computational results demonstrate MO overlapping between neighboring aromatic rings, indicating potential high charge mobility along the  $\pi$ -stacking axes in the solid state (Figure 7). Charge mobility measurement using bottom-gate and bottom-contact OFET testing plat form is under way in our lab.





**Figure 5.** Molecular packing of non-substituted (left), mono-perfluorobutyl substituted (middle), and bis-perfluorobutyl substituted benzophenazines. Dotted blue lines indicate short contact between adjacent molecules.



**Figure 6.** Molecular orbital overlapping in dimer molecules of bis-perfluorobutylated dithiophenazine.

In summary, this project provided solid fundamental understanding to the questions of what type of organic semiconductor materials are suitable for developing air-stable and moisture-resistant flexible optoelectronics. This fundamental solution built a profound basis for the future development of new generation of organic semiconductor devices including but not limit to organic solar cells, OLEDs, OFETs, and electrooptics.

## Bibliography

- [1](a) An, N.; Shi, Y.; Feng, J.; Li, D.; Gao, J.; Chen, Y.; Li, X. *Org. Electron.* **2013**, *14*, 1197-1203; (b) Wei, P.; Menke, T.; Naab, B. D.; Leo, K.; Riede, M.; Bao, Z. *J. Am. Chem. Soc.* **2012**, *134*, 3999-4002; (c) Takeda, Y.; Andrew, T. L.; Lobez, J. M.; Mork, A. J.; Swager, T. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 9042-9046, S9042/9041-S9042/9030; (d) Tan, L.; Guo, Y.; Zhang, G.; Yang, Y.; Zhang, D.; Yu, G.; Xu, W.; Liu, Y. *J. Mater. Chem.* **2011**, *21*, 18042-18048; (e) Gao, X.; Di, C.-a.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697-3699; (f) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *Adv. Funct. Mater.* **2008**, *18*, 1329-1339; (g) Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363-6366; (h) Li, Y.; Tan, L.; Wang, Z.; Qian, H.; Shi, Y.; Hu, W. *Org. Lett.* **2008**, *10*, 529-532.
- [2](a) Song, J.; Kam, F.-Y.; Png, R.-Q.; Seah, W.-L.; Zhuo, J.-M.; Lim, G.-K.; Ho Peter, K. H.; Chua, L.-L. *Nat Nanotechnol* **2013**, *8*, 356-362; (b) Glowatzki, H.; Sonar, P.; Singh, S. P.; Mak, A. M.; Sullivan, M. B.; Chen, W.; Wee, A. T. S.; Dodabalapur, A. *J. Phys. Chem. C* **2013**, *117*, 11530-11539; (c) Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y. *et al. J. Am. Chem. Soc.* **2011**, *133*, 3272-3275; (d) Sirringhaus, H. *Adv. Mater. (Weinheim, Ger.)* **2009**, *21*, 3859-3873; (e) Braga, D.; Horowitz, G. *Adv. Mater. (Weinheim, Ger.)* **2009**, *21*, 1473-1486; (f) Horowitz, G. *Adv. Mater. (Weinheim, Ger.)* **1998**, *10*, 365-377.
- [3](a) Zimmerman Paul, M.; Musgrave Charles, B.; Head-Gordon, M. *Acc Chem Res* **2013**; (b) Clarke, T. M.; Durrant, J. R. *Chem. Rev. (Washington, DC, U. S.)* **2010**, *110*, 6736-6767; (c) Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719-1730; (d) Bredas, J.-L.; Norton, J. E.; Cornil, J.; Coropceanu, V. *Acc. Chem. Res.* **2009**, *42*, 1691-1699; (e) Kawano, K.; Pacios, R.; Poplavskyy, D.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 3520-3530; (f) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924-1945.
- [4](a) Zhu, M.; Yang, C. *Chem. Soc. Rev.* **2013**, *42*, 4963-4976; (b) Seifert, R.; Rabelo de Moraes, I.; Scholz, S.; Gather, M. C.; Luessem, B.; Leo, K. *Org. Electron.* **2013**, *14*, 115-123; (c) Gather, M. C.; Koehnen, A.; Meerholz, K. *Adv. Mater. (Weinheim, Ger.)* **2011**, *23*, 233-248; (d) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Luessem, B.; Leo, K. *Nature (London, U. K.)* **2009**, *459*, 234-238; (e) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556-4573.
- [5](a) Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Koenemann, M.; Erk, P.; Bao, Z. *et al. J. Am. Chem. Soc.* **2009**, *131*, 6215-6228; (b) Forrest, S. R.; Thompson, M. E. *Chem. Rev.* **2007**, *107*, 923-925; (c) Coropceanu, V.; Cornil, J.; Da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J.-L. *Chem. Rev.* **2007**, *107*, 926-952; (d) Guenes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324-1338; (e) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097-1116; (f) Menard, E.; Meitl, M. A.; Sun, Y.; Park, J.-U.; Shir, D. J.-L.; Nam, Y.-S.; Jeon, S.; Rogers, J. A. *Chem. Rev.* **2007**, *107*, 1117-1160; (g) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066-1096; (h) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011-1065; (i) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953-1010; (j) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. *Chem. Rev.* **2007**, *107*, 1233-1271; (k) Zahn, D. R. T.; Gavrila, G. N.; Salvan, G. *Chem. Rev.* **2007**, *107*, 1161-1232; (l) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296-1323; (m) Gates, B. D. *Science (Washington, DC, United States)* **2009**, *323*, 1566-1567; (n) Gates

Byron, D. *Science (New York, N.Y.)* **2009**, 323, 1566-1567; (o) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A. *et al. Nature (London, United Kingdom)* **2002**, 419, 384-387; (p) Lee, M. R.; Eckert, R. D.; Forberich, K.; Dennler, G.; Brabec, C. J.; Gaudiana, R. A. *Science (Washington, DC, United States)* **2009**, 324, 232-235; (q) Feldman, A. K.; Steigerwald, M. L.; Guo, X.; Nuckolls, C. *Acc. Chem. Res.* **2008**, 41, 1731-1741; (r) Oh, J. H.; Suraru, S.-L.; Lee, W.-Y.; Koenemann, M.; Hoeffken, H. W.; Roeger, C.; Schmidt, R.; Chung, Y.; Chen, W.-C.; Wuerthner, F. *et al. Adv. Funct. Mater.*, 20, 2148-2156; (s) Taylor, P. G.; Lee, J.-K.; Zakhidov, A. A.; Chatzichristidi, M.; Fong, H. H.; DeFranco, J. A.; Malliaras, G. G.; Ober, C. K. *Advanced Materials (Weinheim, Germany)* **2009**, 21, 2314-2317; (t) Ahmida, M.; Larocque, R.; Ahmed, M. S.; Vacaru, A.; Donnio, B.; Guillon, D.; Eichhorn, S. H. *J. Mater. Chem.*, 20, 1292-1303; (u) Letizia, J. A.; Cronin, S.; Ortiz, R. P.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *Chem. Eur. J.*, 16, 1911-1928, S1911/1911-S1911/1919; (v) Liu, Y.; Dong, H.; Jiang, S.; Zhao, G.; Shi, Q.; Tan, J.; Jiang, L.; Hu, W.; Zhan, X. *Chem. Mater.* **2013**, 25, 2649-2655; (w) Song, H.-J.; Kim, D.-H.; Lee, E.-J.; Heo, S.-W.; Lee, J.-Y.; Moon, D.-K. *Macromolecules (Washington, DC, U. S.)* **2012**, 45, 7815-7822; (x) Dudenko, D.; Kiersnowski, A.; Shu, J.; Pisula, W.; Sebastiani, D.; Spiess, H. W.; Hansen, M. R. *Angew. Chem., Int. Ed.* **2012**, 51, 11068-11072; (y) Mei, J.; Diao, Y.; Appleton, A. L.; Fang, L.; Bao, Z. *J. Am. Chem. Soc.* **2013**, 135, 6724-6746; (z) Okamoto, T.; Nakahara, K.; Saeki, A.; Seki, S.; Oh, J. H.; Akkerman, H. B.; Bao, Z.; Matsuo, Y. *Chem. Mater.* **2011**, 23, 1646-1649.

[6](a) Jacob, S.; Abdinia, S.; Benwadih, M.; Bablet, J.; Chartier, I.; Gwoziecki, R.; Cantatore, E.; van Roermund, A. H. M.; Maddiona, L.; Tramontana, F. *et al. Solid-State Electron.* **2013**, 84, 167-178; (b) Yun Sun, W.; Kim Jong, H.; Shin, S.; Yang, H.; An, B.-K.; Yang, L.; Park Soo, Y. *Adv Mater* **2012**, 24, 911-915; (c) Geng, Y.; Li, H.-B.; Wu, S.-X.; Su, Z.-M. *J. Mater. Chem.* **2012**, 22, 20840-20851; (d) Wu, Q.; Li, R.; Hong, W.; Li, H.; Gao, X.; Zhu, D. *Chem. Mater.* **2011**, 23, 3138-3140; (e) Chai, S.; Wen, S.-H.; Han, K.-L. *Org. Electron.* **2011**, 12, 1806-1814; (f) Yoo, B.; Jones, B. A.; Basu, D.; Fine, D.; Jung, T.; Mohapatra, S.; Facchetti, A.; Dimmler, K.; Wasielewski, M. R.; Marks, T. J. *et al. Adv. Mater. (Weinheim, Ger.)* **2007**, 19, 4028-4032; (g) Wang, L.; Yoon, M.-H.; Lu, G.; Yang, Y.; Facchetti, A.; Marks, T. J. *Nat. Mater.* **2006**, 5, 893-900.

[7](a) Dong, S.; Zhang, H.; Yang, L.; Bai, M.; Yao, Y.; Chen, H.; Gan, L.; Yang, T.; Jiang, H.; Hou, S. *et al. Adv. Mater. (Weinheim, Ger.)* **2012**, 24, 5576-5580; (b) Martens, S. C.; Zschieschang, U.; Wadepohl, H.; Klauk, H.; Gade, L. H. *Chem. - Eur. J.* **2012**, 18, 3498-3509, S3498/3491-S3498/3493; (c) Sun, H.; Putta, A.; Billion, M. *J. Phys. Chem. A* **2012**, 116, 8015-8022; (d) Usta, H.; Kim, C.; Wang, Z.; Lu, S.; Huang, H.; Facchetti, A.; Marks, T. J. *J. Mater. Chem.* **2012**, 22, 4459-4472.

[8](a) Ebadian, S.; Gholamkhash, B.; Shambayati, S.; Holdcroft, S.; Servati, P. *Sol. Energy Mater. Sol. Cells* **2010**, 94, 2258-2264; (b) Pannemann, C.; Diekmann, T.; Hilleringmann, U. *J. Mater. Res.* **2004**, 19, 1999-2002; (c) Yang, H. B.; Song, Q. L.; Gong, C.; Li, C. M. *Sol. Energy Mater. Sol. Cells* **2010**, 94, 846-849.

[9](a) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, 44, 501-510; (b) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Delimeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, 131, 5586-5608.

[10](a) Jeong, H.-G.; Khim, D.; Jung, E.; Yun, J.-M.; Kim, J.; Ku, J.; Jang, Y. H.; Kim, D.-Y. *J. Polym. Sci., Part A Polym. Chem.* **2013**, 51, 1029-1039; (b) Li, H.; Zheng, R.; Shi, Q. *J. Phys.*

*Chem. C* **2012**, *116*, 11886-11894; (c) Qiao, Y.; Zhang, J.; Xu, W.; Zhu, D. *J. Mater. Chem.* **2012**, *22*, 5706-5714.

[11](a) Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Chemical Communications (Cambridge, United Kingdom)* **2007**, 1003-1022; (b) Ohkubo, K.; Sakamoto, Y.; Suzuki, T.; Tsuzuki, T.; Kumaki, D.; Tokito, S. *Chem. Eur. J.* **2008**, *14*, 4472-4474; (c) Kim, G.; Basarir, F.; Yoon, T.-H. *Synth. Met.* **2011**, *161*, 2092-2096; (d) Lim, Y.-F.; Shu, Y.; Parkin, S. R.; Anthony, J. E.; Malliaras, G. G. *J. Mater. Chem.* **2009**, *19*, 3049-3056.

[12]Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195.

[13](a) Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742-9748; (b) Hoefnagels, H. F.; Wu, D.; de With, G.; Ming, W. *Langmuir* **2007**, *23*, 13158-13163; (c) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science (Washington, DC, U. S.)* **2007**, *318*, 1618-1622.

[14](a) Kiss, L. E.; Kovesdi, I.; Rabai, J. *J. Fluorine Chem.* **2001**, *108*, 95-109; (b) Briza, T.; Kvicala, J.; Paleta, O.; Cermak, J. *Tetrahedron* **2002**, *58*, 3841-3846; (c) Boswell, P. G.; Lugert, E. C.; Rabai, J.; Amin, E. A.; Buehlmann, P. *J. Am. Chem. Soc.* **2005**, *127*, 16976-16984.

[15]Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259-15278.

[16]Sun, H.; Putta, A.; Kloster, J. P.; Tottempudi, U. K. *Chem. Commun.* **2012**, *48*, 12085-12087.

[17](a) Lee, J.-K.; Fong, H. H.; Zakhidov, A. A.; McCluskey, G. E.; Taylor, P. G.; Santiago-Berrios, M. e.; Abruna, H. D.; Holmes, A. B.; Malliaras, G. G.; Ober, C. K. *Macromolecules (Washington, DC, U. S.)* **2010**, *43*, 1195-1198; (b) Fong, H. H.; Lee, J.-K.; Lim, Y.-F.; Zakhidov, A. A.; Wong, W. W. H.; Holmes, A. B.; Ober, C. K.; Malliaras, G. G. *Adv. Mater. (Weinheim, Ger.)* **2011**, *23*, 735-739; (c) Midthun, K. M.; Taylor, P. G.; Newby, C.; Chatzichristidi, M.; Petrou, P. S.; Lee, J.-K.; Kakabakos, S. E.; Baird, B. A.; Ober, C. K. *Biomacromolecules* **2013**, *14*, 993-1002.

[18](a) Sun, H.; Tottempudi, U. K.; Mottishaw, J. D.; Basa, P. N.; Putta, A.; Sykes, A. G. *Crystal Growth & Design* **2012**, *12*, 5655-5662; (b) Mottishaw, J. D.; Sun, H. *J. Phys. Chem. A* **2013**, Just Accepted Manuscript.

[19]Baker, R. J.; Colavita, P. E.; Murphy, D. M.; Platts, J. A.; Wallis, J. D. *J. Phys. Chem. A* **2012**, *116*, 1435-1444.

[20](a) Cametti, M.; Crousse, B.; Metrangolo, P.; Milani, R.; Resnati, G. *Chem. Soc. Rev.* **2012**, *41*, 31-42; (b) Gavette, J. V.; McGrath, J. M.; Spuches, A. M.; Sargent, A. L.; Allen, W. E. *J. Org. Chem.* **2009**, *74*, 3706-3710.

[21](a) Biller, M. J.; Mecozzi, S. *Mol. Phys.* **2012**, *110*, 377-387; (b) Alberti, M.; Aguilar, A.; Lucas, J. M.; Pirani, F. *J. Phys. Chem. A* **2012**, *116*, 5480-5490; (c) Sherrill, C. D.; Sumpter, B. G.; Sinnokrot, M. O.; Marshall, M. S.; Hohenstein, E. G.; Walker, R. C.; Gould, I. R. *J. Comput. Chem.* **2009**, *30*, 2187-2193; (d) DiLabio, G. A. *Chem. Phys. Lett.* **2008**, *455*, 348-353.

[22]Putta, A.; Mottishaw, J. D.; Wang, Z.; Sun, H. *Cryst. Growth Des.* **2014**, *14*, 350-356.

[23]Das, P.; Deng, X.; Zhang, L.; Roth, M. G.; Fontoura, B. M. A.; Phillips, M. A.; De Brabander, J. K. *ACS Med. Chem. Lett.* **2013**, *4*, 517-521.

[24](a) Ando, S.; Nishida, J.-I.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2005**, *17*, 1261-1264; (b) Li, H.; Kim, F. S.; Ren, G.; Hollenbeck, E. C.; Subramaniyan, S.; Jenekhe, S. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 5513-5517; (c) Liang, Z.; Tang, Q.; Liu, J.; Li, J.; Yan, F.; Miao, Q. *Chem. Mater.* **2010**, *22*, 6438-6443.

[25](a) Kang, M. J.; Miyazaki, E.; Osaka, I.; Takimiya, K.; Nakao, A. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2331-2336; (b) Li, X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206-2207.

[26](a) Liang, Y.; Yu, L. *Acc. Chem. Res.* **2010**, *43*, 1227-1236; (b) Osaka, I.; Zhang, R.; Sauve, G.; Smilgies, D.-M.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2009**, *131*, 2521-2529.